THE STRUCTURE OF HETEROPOLYMERS

BY
ROBERT HALL HASEK
B.S., Pennsylvania State College, 1939

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

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Introduction

The polymerization of a mixture of two substituted ethylenic compounds, one of which is readily polymerized alone, but the other is not, will often result in a heteropolymer, which contains both of these units. Such heteropolymers will contain no more than fifty mole per cent of the monomer which is in itself non-polymerizable, which suggests that a 1:1 heteropolymer, or one containing an equal number of both monomeric units, has a structure consisting of alternate units of the two monomers.

The polysulfones, which are heteropolymers of sulfur dioxide and olefins or acetylenes, have been shown to have a "head-to-head, tail-to-tail" type of structure.[1] The object of this investigation was to determine whether the 1:1 heteropolymers of various readily polymerizable vinyl monomers and non-polymerizable 1,2-di-substituted ethylenes, such as maleic anhydride, also had this type of structure.

Discussion of Results

The bulk polymerization of a mixture of vinyl acetate and dibenzoylethylene produced a black solid which was converted by precipitation methods to a light brown powder. Analysis of this material indicated that under the conditions of the polymerization the 1:1 vinyl acetate-dibenzoylethylene heteropolymer had lost two molecules of acetic acid and one molecule of water per double unit (two vinyl acetate and two dibenzoylethylene units, arranged alternately). An adequate explanation of this phenomenon presupposed a "head-to-head, tail-to-tail" type of structure for the heteropolymer. In this structure, the vinyl acetate units are linked "head-to-head" to every other dibenzoylethylene unit, and "tail-to-tail" to the rest. The "head-to-head" acetate groups are in the β-position with respect to the carbonyl groups of the intermediate dibenzoylethylene unit, and are removed, together with the

α-hydrogen atoms of the dibenzoylethylene unit, when acetic acid is eliminated from the heteropolymer. The dibenzoylethylene units linked to the "tails" of the vinyl acetate units are unaffected by this reaction and condense to 2,5-diphenylfuran units, with the resulting loss of one molecule of water per unit. If the vinyl acetate-dibenzoylethylene heteropolymer had a "head-to-tail" type of structure, the elimination of acetic acid would remove one α-hydrogen atom from each dibenzoylethylene unit, and all units would be rendered incapable of furanizing.

The conjugated unsaturation of the heteropolymer was suggested by the dark color of the product and was confirmed by the conversion of the heteropolymer to a colorless product by catalytic hydrogenation. Analysis of the reduction product indicated that the original heteropolymer contained two α,β-unsaturated carbonyl systems and one furan ring per double unit.

The peroxide-catalyzed bulk polymerization of mixtures of vinyl acetate and maleic anhydride and of vinyl acetate and dimethyl fumarate produced the respective 1:1 heteropolymers. The degradation of these products by saponification to a vinyl alcohol-maleic acid heteropolymer, oxidation in alkaline medium to a ketene-maleic acid heteropolymer, and subsequent treatment with alkali at elevated temperatures did not produce isolable quantities of the expected polybasic acids, the identification of which would determine the structure of the original heteropolymers. Oxidation of the vinyl alcohol-maleic acid heteropolymer with nitric acid yielded only a polymeric product.

The polymerization of a mixture of vinylidene chloride and maleic anhydride produced an insoluble black solid, which was partially decarboxylated by acid hydrolysis.

Destructive distillation of a styrene-dimethyl fumarate heteropolymer produced dimethyl fumarate and an unidentified mixture of saponifiable and unsaponifiable material. The ammonium salt of a styrene-maleic acid heteropolymer was oxidized with hydrogen peroxide, but the degradation products were still polymeric in character.

No heteropolymerization occurred when the following mixtures were heated with catalytic amounts of benzoyl peroxide: vinyl acetate-stilbene, vinyl acetate-dimethylmaleic anhydride, methyl methacrylate-dimethylmaleic anhydride, and vinyl acetate- *sym*-dichloroethylene.

References

1. Hunt and Marvel, J. Am. Chem. Soc., **57**, 1691 (1935); Glavis, Ryden and Marvel, *ibid.*, **59**, 707 (1937); Marvel and Sharkey, *ibid.*, **61**, 1603 (1939).

VITA

The author was born in State College, Pennsylvania, June 25, 1918. He attended the State College public schools and high school, and in 1935 matriculated at The Pennsylvania State College, where he received the B.S. degree in chemistry in June, 1939. In September of that same year he entered the Graduate School of the University of Illinois as a teaching assistant in organic chemistry. For the year 1940-41 he was a National Defense Research Assistant, but resumed the position of teaching assistant in 1941-42. He held a University fellowship from September, 1942, to January, 1943.

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